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A review on phase-change materials: Mathematical modeling and simulations

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ABSTRACT

Energy storage components improve the energy efficiency of systems by reducing the mismatch between supply and demand. For this purpose, phase-change materials are particularly attractive since they provide a high-energy storage density at a constant temperature which corresponds to the phase transition temperature of the material. Nevertheless, the incorporation of phase-change materials (PCMs) in a particular application calls for an analysis that will enable the researcher to optimize performances of systems. Due to the non-linear nature of the problem, numerical analysis is generally required to obtain appropriate solutions for the thermal behavior of systems. Therefore, a large amount of research has been carried out on PCMs behavior predictions. The review will present models based on the first law and on the second law of thermodynamics. It shows selected results for several configurations, from numerous authors so as to enable one to start his/her research with an exhaustive overview of the subject. This overview stresses the need to match experimental investigations with recent numerical analyses since in recent years, models mostly rely on other models in their validation stages.

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1. Introduction

The ever increasing level of greenhouse gas emissions combined with the overall rise in fuel prices (although fluctuations occur) are the main reasons behind efforts devoted to improve the use of various sources of energy. Economists, scientists, and engineers throughout the world are in search of (1) strategies to reduce the demand; (2) methods to ensure the security of the supplies; (3) technologies to increase the energy efficiency of power systems; (4) new and renewable sources of energy to replace the limited and harmful fossil fuels.

One of the options to improve energy efficiency is to develop energy storage devices and systems in order to reduce the mismatch between supply and demand. Such devices and systems also improve the performance and reliability by reducing peak loads and allowing systems to work within an optimal range. Thus, they play a preponderant role in conserving energy. The different forms of energy that can be stored are mechanical, electrical, and thermal. Here, mechanical (gravitational, compressed air, flywheels) and electrical (batteries) storages are not considered while thermal energy storage is discussed in the context of latent heat (sensible heat and thermochemical heat are not considered).

Latent heat storage is based on the capture/release of energy when a material undergoes a phase change from solid to liquid, liquid to gas, or vice versa. Latent heat storage is particularly attractive since it provides a high-energy storage density and has the capacity to store energy at a constant temperature – or over a limited range of temperature variation – which is the temperature that corresponds to the phase transition temperature of the material. For instance, it takes 80 times as much energy to melt a given mass of water (ice) than to raise the same amount of water by 1 °C. Table 1 provides a typical comparison between properties of different thermal storage materials used at room temperature. For the interested reader, excellent global reviews that pertain to phase-change materials and their various applications were proposed by Farid et al. [1], Sharma et al. [2], Zhang et al. [3], Regin et al. [4], Tyagi and Buddhi [5], Mondal [6], Sethi and Sharma [7], and especially the recent one by Verma et al. [8].

Nevertheless, the incorporation of phase-change materials (PCMs) in a particular application calls for an analysis that will enable the researcher to determine whether or not PCMs will improve performances sufficiently to justify extra costs for additional systems and/or controls needed. Mathematical modeling of latent heat energy storage materials and/or systems is needed for optimal design and material selection. Therefore, a large amount of research has been carried out on PCMs behavior predictions whether they are considered separately or within specific systems.

Table 1 shows the main differences, on average basis, between sensible heat storage materials and latent heat storage classes of materials. The table indicates that generally, PCMs require much less mass or volume to store the same amount of energy at a more or less constant temperature.

This paper is building on previous reviews [1–8] to update the available references that pertain to mathematical modeling and simulation of thermal energy storage with phase-change materials. First, it presents the fundamental mathematical description of the phenomenon, the Stephan problem. Then, it provides basic mathematical descriptions used as basis for numerical modeling using either first or second law approaches and fixed or adaptative meshes. The next section, considered by the authors as the major contribution, is a model collection of most recent works published on the subject. This survey is organized according to the problem geometry (Cartesian, spherical, and cylindrical) and specific configurations or applications (packed beds, finned surfaces, porous and fibrous materials, slurries). A synthesis is provided at the end and several recommendations are formulated.

2. The Stephan problem

Phase transition of a material is described by a particular kind of boundary value problems for partial differential equations, where phase boundary can move with time. This question has been first studied by Clapeyron and Lamé in 1831 when analyzing the formation of the Earth's crust when it cooled. In that case, the problem was simplified from a spherical geometry to a one-dimensional semi-infinite slab [9]. This solution was found independently by Franz Neumann, who introduced it in his lectures notes of 1835–1840 [10]. Nevertheless, this type of problems is named after Jožef Stefan, the Slovene physicist who introduced the general class of such problems in 1889 [11] in relation to problems of ice formation. Existence of a solution was proved by Evans in 1951 [12], while the uniqueness was proved by Douglas in 1957 [13].

Very few analytical solutions are available in closed form. They are mainly for the one-dimensional cases of an infinite or semi-infinite region with simple initial and boundary conditions and constant thermal properties. Under these conditions, these exact solutions usually take the form of functions of the single variable $x/t^{1/2}$ and are known as similarity solutions [14,15]. A collection of similarity solutions and references is to be found in [16,17].

3. Numerical solution

The problem of predicting the behavior of phase-change systems is difficult due to its inherent non-linear nature at moving interfaces, for which displacement rate is controlled by the latent

Table 1
Common heat storage materials.

Property	Materials			
	Rock	Water	Organic PCM	Inorganic PCM
Density [kg/m^3]	2240	1000	800	1600
Specific heat [kJ/kg K]	1.0	4.2	2.0	2.0
Latent heat [kJ/kg]	–		190	230
Latent heat [MJ/m^3]	–	–	152	368
Storage mass for 10^9 J, avg [kg]	67,000 (Δt = 15 K)	16,000 (Δt = 15 K)	5300	4350
Storage volume for 10^9 J, avg [m^3]	30 (Δt = 15 K)	16 (Δt = 15 K)	6.6	2.7
Relative storage mass	15 (Δt = 15 K)	4 (Δt = 15 K)	1.25	1.0
Relative storage volume	11 (Δt = 15 K)	6 (Δt = 15 K)	2.5	1.0

heat lost or absorbed at the boundary. The following equation, known as the Stephan condition, describes this process:

$$\lambda\rho\left(\frac{ds(t)}{dt}\right) = k_s\left(\frac{\delta T_s}{\delta t}\right) - k_l\left(\frac{\delta T_l}{\delta t}\right), \quad (1)$$

where λ is the latent heat of fusion, ρ is the density (it is not specified if it is solid or liquid), $s(t)$ is the surface position, k is the thermal conductivity, t is time, and T is the temperature. Indexes s and l refers to solid and liquid phases.

In this situation, the position and the velocity of boundaries are not known *a priori*. In addition, since two phases possess different physical properties, this could create the in numerical model non-physical discontinuities which need to be addressed.

3.1. Fixed grid

By introducing an enthalpy method, the phase-change problem becomes much simpler since the governing equation is the same for the two phases; interface conditions are automatically achieved and create a mushy zone between the two phases. This zone avoids sharp discontinuities that may create some numerical instabilities. In consequence, the thickness and the quality of the discretization of this mushy zone are critical to the model performance. The enthalpy method can deal with both mushy and isothermal phase-change problems but the temperature at a typical grid point may oscillate with time [18]. This method has been successfully applied to various phase-change problems [19–22]. Hunter in 1989 [23] and Amdjadi in 1990 [24] confirmed that the enthalpy method is the most suitable for typical applications under the restriction that there is no alteration to the numerical scheme at the interface.

Enthalpy function h, defined as a function of temperature, is given by Voller [25]. For a phase-change process, energy conservation can be expressed in terms of total volumetric enthalpy and temperature for constant thermophysical properties, as follows (from [2]):

$$\frac{\partial H}{\partial t} = \nabla[k_k(\nabla T)], \quad (2)$$

where H is the total volumetric enthalpy, which is the sum of sensible and latent heats:

$$H(T) = h(T) + \rho_1 f(T)\lambda \quad (3)$$

and where

$$h = \int_{T_m}^{T} \rho_k c_k \, dT. \quad (4)$$

In the case of isothermal phase change, the liquid fraction f is given by

$$f = \begin{cases} 0 & T < T_m \quad \text{solid}, \\ ]0,1[& T = T_m \quad \text{mushy}, \\ 1 & T > T_m \quad \text{liquid}. \end{cases} \quad (5)$$

Using Eqs. (3) and (4), one can write an alternate form for dimensional heat transfer in the PCM in two dimensions:

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\left(\alpha\frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(\alpha\frac{\partial h}{\partial y}\right) - \rho_1\lambda\frac{\partial f}{\partial t}, \quad (6)$$

where α is the thermal diffusivity.

Very early, two approaches, finite difference and finite-element techniques, were used to solve the phase-change problems numerically. Then, finite volume and control volume finite-element methods were also employed [26]. Since the introduction of finite-element and finite-volume methods in the 1970s, they are mostly preferred over finite-difference methods.

Since temperature can oscillate with time in some circumstances, some authors have relayed on a temperature based heat capacity method [27]. In these models, the enthalpy-based energy equation is converted into a non-linear equation with a single variable. This approach is called the temperature transforming model (TTM). This type of simulation has proved accurate, simple and efficient [27].

In TTM, general continuity and momentum equations for fluid problems are used. But unlike in the enthalpy formalism, the energy equation uses a temperature dependant source term. The main difficulty of this technique is to develop a method to keep velocity at zero in the solid phase. The simplest method is the *switch-off method* (SOM) or its smoothed version the *ramped switch-off method* (RSOM) [20,28,29]. These techniques directly set velocities in the solid phase to zero by setting coefficients of momentum and velocity-correction equations to values that effectively suppress any motion. Although these methods are commonly used in phase-change problems, Ma and Zhang [18] have shown that if used together with a TTM model for convection controlled solid–liquid phase-change problems, this will result in a serious inconsistency. This is because TTM uses a mushy region to guarantee that the temperature is continuous while in SOM, velocities are discontinuous at the solid–liquid interface. To avoid this discontinuity, a variant of this method uses a ramped switch-off of velocities by introducing a mushy zone between solid and liquid phases.

Instead of modifying coefficients of momentum and velocity-correction equations, an alternate approach modifies the *source term* (STM) in the energy equation at the interface. As SOM, this method also presents a discontinuity at the interface and, therefore, suffers from the same problem. Therefore, a ramped version of this approach should also be used (here RSTM). It should be noted that Darcy STM developed for phase-change simulations in the context of enthalpy method is a type of ramped STM [20,30]. Finally, a third approach is to work with a variable viscosity of the medium (VVM) as proposed by Gartling [31]. In this method, viscosity is set to a very high value in the solid phase, which effectively stops all motions.

Ma and Zhang [18] did a comparison between each of the TTM methods and the experimental results of Okada [32]. They concluded that ramped SOM and ramped STM performed better at a slightly higher computational cost. In addition, they pointed out that if the time step is too small, the convection is not well modeled and that the solutions of the model diverge.

3.2. Adaptive mesh

To keep a reasonable representation of the physical processes that occur at the melt front, model grid density must be high enough to smoothly cover the solid–liquid interface. However, this high density is not needed elsewhere in the numerical domain. Therefore, it is natural to adapt the grid density to the local physical conditions to improve the computational efficiency. There are two main approaches used to do this. One uses a local mesh refinement method, i.e. h-method [33–36]. In this case, the model starts with a uniform grid and, at each iteration, grid points are added or removed to match the required accuracy. This is the method used in most commercial codes. The main problem with this method consists in maintaining data structures since the topology and the number of grid points is changing between each time step.

To avoid this problem, the r-method (r stand for relocation), also known as the *moving mesh method*, starts with a uniform mesh and then moves the mesh points, keeping the mesh topology and number of mesh points fixed as the solution evolves. Grid deformation is usually done by tracking a rapid variation of either the solution or one of its higher order derivatives. This method has been used with phase-change problems as in [37–40].

Lacroix and Voller [41] performed a study comparing methods of simulation of a phase-change model in a rectangular cavity. They concluded that the fixed grid must be finer for a material with a unique melting temperature while the limiting factor in moving mesh is the need to use a coordinate generator at each time increment. Comparison between fixed and moving grid has also be done by Viswanath and Jaluria [42] and by Bertrand et al. [43]. In this last paper, it was found that front-tracking methods are better adapted to the problem than the fixed-grid procedures. The front-tracking methods would however fail to simulate situations where the transition from the liquid to the solid phase is not a macroscopic surface, and enthalpy methods are to be used in most solidification problems where a solid–liquid interfacial region is present between both phases.

3.3. Fist law and second law models

Some models are designed to measure the first law efficiency while others are for the second law. First law models have some shortcomings because they do not consider the effect of time duration through which the heat is stored or retrieved, the temperature at which the heat is supplied, and the temperature of the surroundings. Second law models address those issues which lead to optimal designs and operations. Nevertheless, second law models are intended to complement not replace the first law models.

The first law efficiency of a thermal energy storage system is defined by

$$\eta = \frac{Q_r}{Q_s}, \tag{7}$$

where Q_r is the total thermal energy extracted from the storage material during the heat recovery process and Q_s is the total heat stored by the phase-change material during the heat storage process.

The second law efficiency of the thermal energy storage system is defined by the following equation:

$$\psi = \frac{\phi_r}{\phi_s}, \tag{8}$$

where ϕ_r is the availability recovered from the storage system during the heat recovery process and ϕ_s is the availability added to the system during the heat storage process. This shows that the first law efficiency gauges how energy is utilized, whereas the second law efficiency indicates how well the availability of energy is used.

An important feature in the second law analysis of the thermal energy storage system is the calculation of the entropy generation number N_s. This number is defined as the degraded exergy divided by the total input exergy to the cycle:

$$N_s = \frac{W_d}{W_s + W_r}, \tag{9}$$

where W_d is the total exergy destroyed throughout the cycle, while W_s and W_r, are the availability of the working fluid entering the system during the heat storage and removal processes, respectively. The second law efficiency can be related to the number of entropy generation units by the following equation:

$$\psi = 1 - N_s. \tag{10}$$

In this situation, the system achieves its maximum second law efficiency when N_s is zero.

4. Model collection

In this section, we review the scientific literature on numerical models of PCM used in thermal storage applications. This review is based on compilations by Verma et al. [8] and Regin et al. [4] combined with additional articles found trough a recent literature review. These papers have been first classified by their geometrical configuration for more convenience and then by applications.

4.1. Rectangular geometry

In a pioneer work, Shamsundar and Sparrow [44,45] applied the finite-difference method to the resolution of the enthalpy equation in the solidification of a flat plate. Shamsundar also used this method to the case of a square geometry [46–48].

Hamdam and Elwerr [49] presented a simple model where all sides of a rectangular enclosure were well insulated except one vertical side where heat was applied. In this model, the rate of melting depends essentially on the properties of the material, such as thermal diffusivity, viscosity, conductivity, latent heat of fusion and specific heat. The model follows a two-dimensional melting process of a solid PCM considering convection as the dominant mode within the melt region, except within the layer very close to the solid boundary in which only conduction is assumed to take place. Comparison between this model and results of Bernard et al. [50] shows a good agreement except that position and inclination of the melt front deviate as time progresses.

Lacroix et al. [51–54] solved the problem of fusion in a rectangular cavity including the natural convection effects using a methodology similar to the moving mesh technique. Results of these simulations indicate that the melted fraction from close-contact melting at the bottom of the cavity is larger, by an order of magnitude, than that from the conduction dominated melting at the top. The melting process is essentially governed by the magnitude of the Stefan number. It is also strongly influenced by lateral dimensions of the cavity. The importance of the convection also implies that system efficiency is increased when the heat is concentrated on few spots instead of being spread over the whole surface. Later Brousseau and Lacroix [55,56] studied performances of a multi-layer PCM storage unit. Their model is based on the conservation equation of energy for the PCM and for the HTF (heat-transfer fluid). This model shows that cyclic melting and solidification yields complex isotherm distributions within the PCM with multiple phase fronts.

Works by Costa et al. [57] studied numerically a two-dimensional rectangular area, using energy equations in solid and liquid phases, continuity, momentum, and Stefan's equation at the boundary. They applied the enthalpy-porosity approach used by Voller et al. [30,250] to the governing equations. Three PCMs were analyzed: paraffin (n-octadecanol) and metals (gallium and tin). They compared their results with those obtained in the literature [245–249]. In the case of octadecanol, there is poor agreement with experimental results in the upper zone where melt liquid from the sides fills the upper empty cavity and accelerates melting in this area. Variation of viscosity with temperature, heating losses in the wall or different initial supercooling are proposed explanations for this discrepancy [57,58].

Since most PCMs have low thermal conductivities, then heat-transfer rates limit their applications. To improve their performances they are often used in a thin plate configuration like a heat exchanger [59–64]. Costa et al. [65] also studied a thermal storage system consisting of seven thin rectangular containers of PCM. The shape of the container is used to enhance the rate of heat transfer. The performance of this system has been analyzed using an enthalpy formulation and a fully implicit finite-difference method [25,66]. Vakilaltojjar and Saman [67] proposed to improve on this design by using PCM with different melting point ($CaCl_2$–$6H_2O$ and potassium fluoride tetrahydrate (KF–$4H_2O$).

Dolado et al. [68] developed a model for thermal energy storage unit for air conditioning application using thin PCM slab. In

parallel, they have also characterized the PCM in laboratory as well as experimentally validated their model. Comparing various numerical approaches, they showed that a simple 1D implicit finite differences model seems to be an appropriate model to simulate both, single PCM slabs and full storage systems. Comparing the advantages of various numerical approaches, they concluded that semi-analytical models give a fast first approach, successful to optimize the design, while 2D model should be used to study thicker plates and that the complete computational fluid dynamics model should be employed for more rigorous analyses.

Zukowski [69] has analyzed the heat and mass transfer in a ventilation duct filled with encapsulated paraffin wax RII-56. This author proposed a new approach for approximating the specific heat of the PCM as a function of its temperature for the whole range of operating conditions, by using an interpolating cubic spline function to estimate specific heat of PCM at each temperature. His analysis showed that the average charge time (melting) of the tested units was over twice higher than the time of the discharge cycle (freezing).

Silva et al. [70] have modeled an enclosure filled with wax in a rectangular geometry oriented vertically. Their results show that a simplified numerical model can be used to predict, with reasonable accuracy, the performance of this kind of heat exchange unit. Vynnycky and Kimura [71] produced an analytical and numerical study of coupled transient natural convection and solidification in a rectangular enclosure. Their work, based on a non-dimensional analysis, indicates that some asymptotic simplification is possible for materials commonly used in literature (water, gallium, lauric acid). This suggests that problems might be simplified, when $Ra \gg 1$ and $St \ll 1$, giving a conventional boundary value problem for the liquid phase and pointwise-in-space first-order ordinary differential equations for the evolution in time of the solidification front. The method was tested against full 2D finite-element-based transient numerical simulations of solidification. The asymptotic analysis decouple the fluid flow and heat-transfer problem in the liquid from the heat-transfer problem in the solid, and is able to describe the quantitative features of the numerical solutions very well for about 90% of the height of the enclosures. However, in the final 10%, the analytical solution is not uniformly valid for all time, and tends to overestimate the final thickness of the solid layer.

Zivkovic and Fujii [72] have created a simple computational model for isothermal phase change. The model was based on an enthalpy formulation with equations constructed in such a form that the only unknown variable is the PCMs temperature. The theoretical model was verified with a test problem and an experiment performed by authors. Experimental and computational data demonstrated that heat conduction within the PCM in the direction of the fluid flow, the thermal resistance of the container's wall, and the effects of natural convection within the melt could be ignored for the conditions investigated in this study. This model also shows that the rectangular container requires nearly half of the melting time as for the cylindrical container with the same volume and heat-transfer area. Using the same formalism, Najjar and Hasan [73] built a model of a greenhouse using a PCM as a heat storage unit. They validate their model by comparison with the experimental results of [72].

Other studies have also explored the behavior of PCM in rectangular geometries [74,75]. They are not explicitly reviewed herein but provided for the interested reader. Table 2 presents a summary of numerical methods used in the context of the Cartesian coordinates system. The symbols FG stand for fixed grid, FD for finite difference, FE for finite element, A for analytic, CFD for computed fluid dynamics and MM for moving mesh respectively.

Table 2
Models for rectangular geometry.

Model	Material	Numerical formulation		Comment	Validation
Shamsundar and Sparrow [44,45]		FD	2D	Surface integrated heat-transfer rates; boundary temperatures solidified fraction and interface position all as function of the time	
Hamdam and Elwerr [49]	n-Octadecane	A	1D	Propagation and inclination of the interface and energy storage rate predicted	Experimental [50]
					Numerical [214,215]
Lacroix et al. [51–54]	n-Octadecane [51]	FG	2D	The melting process is chiefly governed by the magnitude of the Stefan number	Experimental [53,246]
					Numerical [16]
Brousseau and Lacroix [55,56]		FD	2D	Multi-layer PCM storage	Numerical [251]
		FG		Parametric model formulated from numerical study	
Costa et al. [57]	n-Octadecanol gallium, tin	FD	2D	For n-octadecanol, there is poor agreement with experimental results. Variation of viscosity with temperature, as heating losses in the wall or different initial supercooling are the proposed explanation for this discrepancy	Experimental [245–249]
Costa et al. [65]	Multiple PCM	FD	1D	For 1D model, calculations have been made for the melt fraction and energy stored for conduction and convection, while for 2D model, calculations have been made for conduction only.	Numerical [216,217]
			2D		
Vakilaltojjar and Saman [67]	$CaCl_2$–$6H_2O$	A	2D	Thin flat containers and air is passed through gaps between them	On going, not published
	KF–$4H_2O$	FE			
Dolado et al. [68]		A	1D	Encapsulated PCM slab	Experimental [218]
		FD	2D		
		CFD			
Zukowski [69]	Paraffin wax RII-56	FD	3D	Interpolating cubic spline function method is used for determining an effective specific heat	Yes
Silva et al. [70]	Paraffin wax	MM	1D	Charge and discharge of a PCM encapsulated slab	Yes
Vynnycky and Kimura [71]	Lauric acid	MMLE*	2D	Laplace–Euler: new numerical method*	Experimental [116]
				Applicable to water and gallium	Numerical [219]
Zivkovic and Fujii [72]	$CaCl_2$–$6H_2O$	FD	1D	Isothermal phase change of encapsulated PCM	Yes
					Numerical [25]

4.2. Spherical geometry

Spherical geometry represents an interesting case for heat storage application, since spheres are often used in packed beds as those described in Section 4.4. Due to the complexity of such systems, it is often more efficient to first model the behavior of an individual sphere, to then describe it with a simple parametric model to be used in the packed bed modeling.

Roy and Sengupta [76] have examined the melting process with the solid phase initially uniformly supercooled. The presence of supercooling, forced them to modify the heat-transfer equation to include the effects of a temperature gradient in the solid core. As a result, a closed-form solution could not be obtained. At every time step, the unsteady conduction equation has been solved numerically using a toroidal coordinate system, which has been suitably transformed to immobilize the moving boundary and to transform the infinite domain into a finite one. In a subsequent paper [77], they have examined the impact of convection on the melting process. They demonstrated that the fluid flow in the upper liquid region is essentially quasi-steady, since the liquid velocity in both the film and the upper zone are much greater than the rate of movement of the interface. They also demonstrated the importance of the ratio of the buoyancy force due to density variation of the liquid with temperature, and the density difference between the two phases, which reduces the melt rate and places an upper bound for the range over which the film solution is valid.

Ettouney et al. [78] experimentally evaluated the heat transfer in paraffin inside spherical shell. Their calculation shows that the Nusselt number in the phase-change material during melting is one order of magnitude higher than during solidification and is strongly dependent on the sphere diameter. In consequence, the melting was about a factor two slower than the freezing. This counter-intuitive behavior is caused by the convection, which brings a large fraction of the heat to the upper part of the sphere, where it heats the melt fraction instead of the solid phase. In the freezing process, conduction dominates and the freezing occurs around the entire surface. As the melt volume decreases and the role of natural convection diminishes rapidly. This result contrasts with the work of Barba and Spriga [79] on the behavior of encapsulated salt hydrates, used as latent energy storage in a heat-transfer system of a domestic hot water tank, who found that the shortest time for complete solidification is provided by small spherical capsules, with high Jacob numbers and thermal conductivities. On the impact of convection, Khodadadi and Zhang [80] also noted that it created an asymmetry: melting in the upper region of the sphere much faster than in the lower region due to the enhancement. Their computational findings were verified through qualitative constrained melting experiments using a high-Prandtl number wax as the phase-change material.

A simple analytical solution was derived by Fomin and Saitoh [81] to describe close-contact melting within a spherical capsule. Its accuracy is estimated to be 10–15% by comparison to numerical analysis. This tool is likely to be useful when evaluating thermal energy storage systems which contain thousands of capsules. A similar analysis has been done for elliptical capsule. It was found that elliptical capsules show higher rate of melting than circular ones. Prolate capsules provide more effective melting than oblate ones, even though they have the same aspect ratios and vertical cross-sectional areas [82,83]. In addition, Adref and Eames [84,85] have been able to derive semi-empirical equations that allow the mass of ice within a sphere to be predicted during the freezing or melting processes. Complementary studies on quasi-static models and on parametric models have been done by others research teams [86–90].

Ismail and Henriquez [88] created a parametric model for the study of the solidification of a PCM in a spherical shell. This model was based on pure conduction in the PCM subject to boundary conditions of constant temperature or convection heat transfer on the external surface of the spherical shell. The model was validated by comparison with available similar models [91–94] and the agreement was found to be satisfactory. Like other groups, they found that the increase of the size of the sphere leads to increasing the time for freezing. The same team performed a specific numerical and experimental study on water solidification [89]. The governing equations of the problem and associated boundary conditions were formulated and solved using a finite-difference approach and a moving grid scheme. A shortcoming of the model was its incapacity of adequately handling supercooling. Nevertheless, they conclude that shell material affects the solidification time. Freezing was faster for metallic material (Cu, Al) followed by polyethylene, acrylic and PVC. However, the time difference was rather small, which still makes non metallic capsules attractive.

Veerappan et al. [95] did a an investigation the phase-change behavior of 65 mol% capric acid and 35 mol% lauric acid, calcium chloride hexahydrate, n-octadecane, n-hexadecane, and n-eicosane inside spherical enclosures. They compared their numerical model results with the experimental work of Eames and Adref [96] and they concluded with a good agreement between them, notwithstanding the fact that Eames and Adref [96] worked with ice which floats unlike solid phase of modeled PCMs. Based on their modeling, they found that spheres with larger diameters take more time to completely solidify than smaller diameters ones, since heat has to travel a smaller distance and hence rate of solidification is higher for smaller capsules. The same is true for melting. However, both freezing and melting took approximately the same time, which contrasts with result of [69,78].

Regin et al. [97] carried out both an experimental and numerical analysis of a spherical capsule placed in a convective environment filled with wax as a PCM. Model results were compared to experimental results and were found to be in good agreement. From the model results, they found that the shorter time for complete melting and higher time averaged heat flux occurs in the capsules of smaller radii and for higher Stefan number.

Lin and Jiang [86] developed an improved quasi-steady analysis model for freezing in a slab, a cylinder, and a sphere. Their improvement was the introduction of an additional term to the temperature profile to simulate the transient effect on the temperature distribution in the solid phase. This additional term is based on the ratio of the heat flux at the phase boundary to that at the cooling surface, and physically, represents the thermal capacity effect in the frozen region. The maximum relative error of the moving phase front location obtained from the improved quasi-steady analysis of a slab is about 3% in comparison with that obtained from the exact solution of the freezing process in a slab, while the error for the classical quasi-steady analysis is 20%. Since there is no exact solution available for the freezing process taking place in a cylinder or a sphere, the results obtained from the improved quasi-steady analysis are compared with results of [92,98–102] compiled by Lunardini [103]. For these geometries, the maximum relative errors of the improved quasi-steady analysis are less than 4%, while the maximum relative errors of the quasi-steady approximation are higher than 42%. In addition to this improvement in precision, the improved model is also less sensitive to the variation of Stephan numbers.

Bilir and Ilken [87] have investigated the solidification problem of a phase-change material encapsulated in a cylindrical/spherical container. The governing non-dimensional form of equations of the problem and boundary conditions were formulated and solved numerically by using enthalpy method with control volume approach. The numerical code was validated through comparison with results of other authors [88,101,104]. In general, there is a good agreement. The small differences are due to the omission of the thermal resistance of the container and the time dependency of

the convection coefficient. Since convection increases with the size of the container, differences get larger as the sphere diameter increases. Running the simulations for various Stefan and Biot numbers and superheat parameter, they produced a regression which enables them to determine the coefficient of a function predicting the freezing time. The coefficient of correlation of this regression is 0.996, which makes it suitable for solving engineering problems.

Assis et al. [90] produced a parametric investigation of melting in spherical shells. Their simulations incorporated such phenomena as convection in the liquid phase, volumetric expansion due to melting, sinking of the solid in the liquid, and close-contact melting. Their model attempts to solve complete transient conservation equations simultaneously for solid PCM, liquid PCM, and air, while allowing for PCM expansion, convection in the fluid media (melted PCM and air), and solid phase motion in the liquid in a similar way as in [105]. This numerical simulation compares favorably with results of the experimental investigation based on previous work by the same group [106,107].

Khodadadi and Zhang [80] performed a computational study of the effects of buoyancy-driven convection on constrained melting of phase-change materials within spherical containers. They found that, early during the melting process, conduction was dominant. As the buoyancy-driven convection is strengthened due to the growth of the melt zone, melting in the top region of the sphere is much faster than in the bottom region due to the enhancement of the conduction mode of heat transfer. They noted that the intensity of natural convection is more clearly indicated by the Rayleigh number than the Stefan number, as the flow pattern and overall convective effects change markedly with the Rayleigh number. These numerical findings were backed by an experimental visualization of the melting of a commercial grade wax inside spherical bulbs.

Tan et al. [108,109] carried out a similar work on constrained melting of phase-change materials to impend the fall of solid phase at the bottom of the container. Paraffin wax (n-octadecane) was constrained, through the use of thermocouples, during melting inside a transparent glass sphere. Their experimental setup provided detailed temperature data that were collected during the course of the melting process along the vertical diameter of the sphere. They pointed out that experimental setup underestimates the waviness and the excessive melting of the bottom of the PCM compared to numerical predictions. They concluded that this discrepancy could be caused by the support structure required to hold the sphere, since it could have inhibited heat from reaching the bottom of the sphere.

Table 3 presents the synthesis for the analyses in spherical geometries.

4.3. Cylindrical geometry

Anica Trp [110,111] analyzed the transient heat-transfer phenomenon during technical grade paraffin melting and solidification in a cylindrical shell. The mathematical model, formulated to represent the physical problem, has been proved suitable to treat both melting and solidification processes. It can be concluded that the selection of the operating conditions and geometric parameters dimensions depends on the required heat-transfer rate and the time in which the energy has to be stored or delivered. In consequence, these parameters must be chosen carefully to optimize thermal performances of the storage unit.

Gong and Mujumdar [112] developed a finite-element model for an exchanger consisting of a tube surrounded by an external co-axial cylinder made up of PCMs. This model compares characteristics of two operation modes. In mode 1, hot and cold fluids are introduced from the same end of the tube whereas in mode 2, hot and cold fluids are introduced from different ends. Analyses show that the energy charged or discharged in a cycle using mode 1 is 5.0% higher than when using mode 2. The charge/discharge rate is also faster when using mode 1 because the temperature difference between the fluid and the PCM is higher in the fluid inlet than in the outlet. The larger the temperature difference is the more deeply the phase-change interface penetrates into the PCM and the more heat is stocked. In the discharge process, symmetrical phenomena occur.

El-Dessouky and Al-Juwayhel [113] presented a technique to predict the effect of different designs and operating parameters on the entropy generation number or the second law effectiveness of a latent heat thermal energy storage system (LHTES) where the PCM is contained in the annulus of a double-pipe heat exchanger. One of the conclusions of this analysis is that second law effectiveness increases with the increase of Reynolds's number, specific heat-

Table 3
Models for spherical geometry.

Model	Material	Numerical formulation		Comment	Validation
Roy and Sengupta [76]		MM FD	2D	Treatment of convection Two zones model	Numerical [220]
Barba and Spriga [79]	37.5% NH_4NO_3 + 62.5% $Mg(NO_3)\cdot 6H_2O$	A	1D	Transient position of interface, temperature distribution, melting fraction, energy released, and duration of complete solidification	No
Fomin and Saitoh [81]	n-Octadecane	A	2D	Contact melting on unfixed solid phase	Experimental [221] Numerical [222,223]
Adref and Eames [84,85]	Ice			Capsule filled a 80% with an air cell on the top	Eames and Adref [96]
Ismail and Henriquez [89]		MM FD	1D	Numerical correlation relating the working fluid temperature to the time has been produced	Numerical [91–94]
Ismail, Henriquez and da Silva [88]	Ice	MM FD	1D	Analysis of the impact of thermal conductivity of the shell material	Yes
Veerappan et al. [95]	Various PCM	A	2D	Solidification and melting of sphere with conduction, natural convection, and heat generation	Experimental [96]
Regin et al. [97]	Paraffin wax	FD		Convective environment outside capsule	Yes
Lin and Jiang [86]		A	1D	Quasi-steady analysis	Numerical [92,98–102]
Bilir and Ilken [87]		FG	1D	Correlations which express the dimensionless total solidification time of the PCM in terms of Stefan Number, Biot Number and Superheat Parameter were derived	Numerical [88,101,104]
Assis et al. [90]	Parrafin wax RT27	MM	2D	Partly filled capsule with open end	Yes + experimental [106,107]
Khodadadi and Zhang [80]	Beewax	CFD FG	2D	Constrained melting	Yes
Tan et al. [108]	n-Octadecane	MM CFD	2D	Constrained and unconstrained melting	Experimental [109]

transfer area and operating fluid wall temperature in the heat recovery process and with the decrease of fluid inlet temperature in the heat storage process.

For a solar water heater, Prakash et al. [114] analyzed a storage unit containing a layer of PCM at the bottom. Bansal and Buddhi [115] did the same thing for a cylindrical storage unit in the closed loop with a flat plate collector. In an effort to improve performances of phase-change storage units for solar heating applications, Farid [116] has suggested using many PCM with different melting temperatures. This idea has been applied later by Farid and Kanzawa [117] and Farid et al. [118] for a unit consisting of vertical tubes filled with three types of waxes having different melting temperatures. During heat charge, the air flows first across the PCM with the highest melting temperature to ensure continuous melting of most of the PCM. The direction of the air flow must be reversed during heat discharge. Both the theoretical and experimental measurements showed an improvement in performances of the phase-change storage units using this type of arrangement.

Jones et al. [119] performed well-controlled and well-characterized experimental measurements of melting of a moderate-Prandtl-number material (n-eicosane) in a cylindrical enclosure heated from the side. The melt front was captured photographically and numerically digitized. A numerical comparison exercise was undertaken using a multi-block finite-volume method and the enthalpy method for a range of Stefan numbers. Very good agreement was obtained between the predictions and the experiments for Stefan numbers up to 0.1807.

Esen and Ayhan [120] developed a model to investigate the performance of a cylindrical energy storage tank. In the tank, the PCM was packed in cylinders and HTF flowed parallel to it. The PCMs considered were calcium chloride hexahydrate ($CaCl_2$–$6H_2O$), paraffin wax (P-116), Na_2SO_4–$10H_2O$ and paraffin. The performance of cylindrical energy storage tank was determined by computer simulations [121,122] and backed by experimental data. The results show that the stored energy becomes higher at a given time as the mass flow rate or inlet HTF temperature increases and for more energy storage appropriate cylinder wall materials and dimensions should be selected, such as higher thermal conductivity and small radius.

Jian-you [123] produced a numerical and experimental investigation of a thermal storage unit involving a triplex concentric tube with PCM filling in the middle channel, with hot heat-transfer fluid flowing into the outer channel during charging process and cold heat-transfer fluid flowing into the inner channel during discharging process. A simple numerical method, according to energy conservation, called temperature and thermal resistance iteration method has been developed for the analysis of PCM solidification and melting in the triplex concentric tube. Comparison between numerical predictions and the experimental data shows good agreement.

Table 4 presents a complete picture at a glance of numerical methods in cylindrical geometries.

4.4. Packeds beds

Since most PCMs possess a low thermal conductivity, increasing surface/volume ratio is appealing to increase the heat-transfer rate. This can be done by packing a volume with a large number of PCM capsules. Saitoh and Hirose [124] put in evidence this idea both theoretically and experimentally. However, this improvement comes at the price of a significant pressure drop and a higher initial cost.

Zhang et al. [125] produced a general model for analyzing thermal performances of both melting and solidification process of a LHTES composed of PCM capsules. This model can be used to analyze the instantaneous temperature distribution, the instantaneous heat-transfer rate, and the thermal storage capacity of LHTES system. From this modeling effort, it was found that the thermal performance of a given system can be determined by the effective filling factor of a PCM capsule. Since formulation of the effective filling factor for given geometric and flow conditions are available in the literature [1,126–128], this largely reduces complexity of calculation. This model was validated with the results in literature for a LHTES composed of PCM spheres. The model is quite general so it can be used to optimize and to simulate the thermal behavior of LHTES.

Benmansour et al. [129] developed a two-dimensional numerical model that predicts the transient response of a cylindrical packed bed randomly packed with spheres of uniform sizes and encapsulating paraffin wax with air as a working fluid. Experimental measurements of temperature distribution compared favorably with the numerical results over a broad range of Reynolds numbers and showed that the time at which the bed reaches the thermal saturation state decreases significantly with the mass flow rate of air.

Bédécarrats et al. [130–136] worked on a model of a cylindrical tank filled with encapsulated phase-change materials. This model had the particularity of examining the impact of supercooling, which can seriously deteriorate performances of a LHTES [131,132]. Numerical results were validated with an experimental test tank. From both numerical and experiment results, it was found that the optimum charging mode is obtained in the case of the vertical position, where the motions due to the natural convection, are in the same direction as the forced convection. Also, they demonstrated that an increase in flow rate increases the charge and the discharge rates. They also recommend to slightly oversize the tank.

Cheralathan et al. [137] did also a numerical and experimental study of the impact of super cooling and porosity. They came to the conclusion that lower inlet HTF temperature reduces the supercooling of the PCM and the total charging time. However, the

Table 4
Models for cylindrical geometry.

Model	Material	Numerical formulation		Comment	Validation
Trp [110,111]	Parafin wax RT 30	FG	2D	Melting + solidification	Yes
Gong and Mujumdar [112]	80.5% LiF + 19.5% CaF_2	FG	2D	Co-axial exchanger	No
El-Dessouky and Al-Juwayhel [113]	Parafin wax, $CaCl_2$–$6H_2O$	A	2D	Second law	No
Prakash et al. [114]		M	2D	Vertical cylinder with PCM at the bottom	Yes
Bansal and Buddhi [115]		MM	2D	Closed loop with a flat plate collector	Yes
Farid and Kanzawa [117]		MM	2D	Several MCPs with different melting temperatures	Yes
Jones et al. [119]	n-Eicosane	MM	2D	Multi-block FVM	Yes
Esen and Ayhan [120]	$CaCl_2{\cdot}6H_2O$ paraffin, $Na_2SO_4{\cdot}10H_2O$ paraffin	FD FG	2D	Energy storage reservoir	Experimental [224]
Jian-you [123]	n-Hexacosane		1D	Triplex concentric tube Temperature and thermal resistance iteration method	Yes

reduction of heat-transfer fluid temperature also reduces the performance of the refrigeration system. Therefore, there is a trade to do between inlet temperature and overall performances. Low porosity increase storage capacity of the system at the expense of a slower charging/discharging rate.

Arkar and Medved [138] also studied a cylindrical container containing spheres filled with paraffin. Their model was adapted to take into account the non-uniformity of porosity and the fluid velocity. Both are the consequence of a small tube-to-sphere diameter ratio of their system. A comparison of the numerical and experimental results confirmed the important role of PCMs thermal properties especially during slow running processes.

Wei et al. [139] explored the impact of geometry (sphere, cylinder, plate and tube) of capsules on packed bed performances. Effects of the capsule diameter and shell thickness and the void fraction were also investigated. They discovered that the heat release performance decreases in the order from sphere, to cylinder, to plate and finally to tube. Working on another aspect of system optimization, Seeniraj and Lakshmi Narasimhan [140] study considered the impact of heat leak through sidewalls by convection. Their results indicate a significant delay in the solidification process with a relatively lower charging rate for the LHTS unit with convective heat leak. Based on this result, they derived limiting values of heat leak ratio for effective charging of these systems.

Ismail and Henriquez [141] have created a simplified transient one-dimensional model of PCM capsule stocked in a cylindrical tank. The convection present in the liquid phase of the PCM is treated by using an effective heat conduction coefficient. The solution of the differential equations was realized by the finite-difference approximation and a moving mesh inside the spherical capsule. The geometrical and operational parameters of the system were investigated both numerically and experimentally and their influence on the charging and discharging times was investigated. Ismail and Stuginsky [142] compared four basic groups of models of packed beds: the continuous solid phase models, Schumann's model, the single phase models and the thermal diffusion models. Numerical tests were carried out to evaluate the time consumed by each of them. It was found that these models were essentially equivalent except for the computational time. For example, model with a thermal gradient inside the solid particles needed more than twenty times the computing resources required by Schumann's model.

Chen [143,144] also developed a one-dimensional porous-medium model. Predictions of this model were compared with the lumped capacitance model which assumes a uniform temperature in the packed capsules and in the coolant flow and with experimental data derived from literature. Results show that the one-dimensional model has the advantage of predicting the temperature distributions of PCM and coolant. For the study of transient response of PCM beds, Gonçalves and Probert [145] have introduced a new non-dimensional number, the Gonçalves number, which mean integrated value can be used to characterize the thermal response of a thermal energy storing system.

Adebiyi et al. [146] have developed a model of a packed bed for high-temperature thermal energy storage that incorporates several features: thermal properties variations with temperature, provisions for arbitrary initial conditions and time-dependent varying fluid inlet temperature, formulation for axial thermal dispersion effects in the bed, modeling for intraparticle transient conduction, energy storage in the fluid medium, transient conduction in the containment vessel wall. Energy extraction can be achieved either with flow direction parallel to that in the storage mode (concurrent) or in the opposite direction (counter-current). This model also allows the computation of the first and second law efficiencies. Yagi and Akiyama [147] have also studied the heat-transfer problem at high temperatures. Six different materials were tested as PCMs: two inorganic and four metallic materials. The metal PCMs were found to be excellent for heat storage because of uniform temperature in the capsule. Heat-transfer simulation was also conducted for a packed bed process of spherical capsules and concurrent flow for heat storage and release showed better result for effective use of storage heat than counter-current flow.

Wanatabe et al. [148,149] have explored the impact of combining PCMs with various melting points on exergy efficiency and charging and discharging rates in a latent heat storage system. The heat storage module consisted of horizontal cylindrical capsules filled with three types of PCMs. The optimum melting point distribution of the PCMs has been estimated from numerical simulations and also from simple equations. The fast charging or discharging rate leads to high exergy efficiency. Both the experimental and numerical results showed some improvement in charging and discharging rates by use of multiple PCMs.

MacPhee and Dincer [150] studied the melting and freezing of water in spherical capsules using ANSYS, GAMBIT, and FLUENT 6.0. These models were validated through a rigorous time and grid independence tests and their numerical results were successfully compared to the experimental ones of [78]. Energy efficiency was calculated and found to be over 99%, though viscous dissipation was included. Using exergy analysis, the exergetic efficiencies are determined to be about 75% to over 92%, depending on the HTF scenario. The two efficiencies decreased when hot transfer fluid flow was increased, due mainly to increasing heat losses and exergy dissipation. These results are different from those obtained by Wanatabe et al. [148,149]. Higher temperature differences between hot fluid and melting temperature of PCMs were found to be most optimal exergetically, but least optimal energetically due to entropy generation accompanying heat transfer. Higher temperature differences also increased the rates of charging/discharging. However, increasing the HTF flow rate did not decrease the charging and discharging times by any relatively significant amount. This result is somewhat discrepant with various previous studies [129–136]. The same team also developed a simple analytical model [151] that describes heat transfer, fluid flow, and thermodynamic, which brought essentially the same conclusions as the numerical model.

A summary for packed beds models is provided in Table 5.

4.5. Finned geometry

Another approach to increase the heat exchange efficiency in PCMs is to use fins in the heat exchange system. These somehow more complex geometries have been extensively studied.

Sasaguchi et al. [152,153] studied experimentally and theoretically effects of the configuration of a finned tube on the heat-transfer characteristics of a latent heat thermal energy storage system. They concluded that performance of the unit is almost the same for any configuration with the same surface area even if it is quite different.

Lacroix [154] developed a theoretical model, using an enthalpy-based method coupled to a convective heat transfer of a shell-tube thermal storage unit with PCM on the shell side and the HTF circulating inside the tubes. The numerical model was validated through comparison with experimental data. In addition, comparison was done between models of bare and finned tubes. Results showed that the annular fins are the most effective for moderate mass flow rates and small inlet temperatures. Lacroix and Benmadda [155] also studied the behavior of a vertical rectangular cavity filled with PCM. They used a fixed-grid model which was validated with experimental data. They found that both solidification and melting rates were improved by long fins. However, melting rates reach a maximum when the number of fins is increased since they interfere with the convection.

Zhang and Faghri [156] studied the heat-transfer enhancement produced by externally finned tube in a latent heat energy storage system. The heat conduction in the tube wall, fins and the PCM

Table 5
Models for packed bed.

Model	Material	Numerical formulation		Comment	Validation
Zhang et al. [125]		A	1D	A general model, great reference paper	Numerical [225–229]
Benmansour et al. [129]	Parafin wax	FD	2D	Mass flow rate is determinant	Yes
Bédécarrats et al. [130–136]		PM	2D	Supercooling studied	Experimental [131,135,230]
Cheralathan et al. [137]	Ice		1D	Supercooling is reduced by lower inlet HTF temperature	Yes
Arkar and Medved [138]	Parafin wax RT20	PM FD FG	2D	Continuous solid phase model	Yes
Wei et al. [139]	Paraffin wax FNP-0090	FD FG	1D	Geometry analysis of capsules	Yes
Seeniraj and Lakshmi Narasimhan [140]				Heat leaks through sidewalls	Experimental [144]
Ismail and Henriquez [141]	Ice	FD MM	1D	Effective heat conduction coefficient	Yes
Ismail and Stuginsky [142]			1D	Parametric model	
Chen [143,144]	Ice		1D	Solution by Laplace transform	Experimental [144]
Goncalves and Probert [145]	$MgCl_2{\cdot}6H_2O$			Their own dimensionless number!	Yes
Adebiyi et al. [146]	ZrO_2 Cu			First and second law efficiency, high temp	Yes
Yagi and Akiyama [147]	KNO_3–$NaNO_3$ NaCl, Pb Al–Si		1D	Six materials with various melting points	Yes
Wanatabe et al. [148,149]			1D	Second Law model	Yes
MacPhee and Dincer [150]			2D	First and second law efficiency. Fluent	Experimental [78]

were described by a temperature transforming model using a fixed-grid numerical method [27]. This model assumes that the melting process occurs over a range of phase-change temperatures, but it also can be successfully used to simulate the melting process occurring at a single temperature by taking a small range of phase-change temperature. This model was validated through comparison with Lacroix [154] and agreement between the two was found to be quite good. The results show that the local Nusselt number inside the tube cannot be simply given by the Graetz solution. The model also shows that transverse fins are a more efficient way to enhance the melting heat transfer if the initial subcooling exists in the PCM. The height of the fins has significant effect on the melting front on the two sides of the fins but has no significant effect on the melting front between the transverse fins.

Velraj et al. [157] studied the impact of internal longitudinal fins on a cylindrical vertical tube filled with paraffin. A theoretical model that accounts for the circumferential heat flow through the tube wall was developed using enthalpy formulation and was employed in conjunction with the fully implicit finite-difference method to solve the solidification in the convectively cooled vertical tube. They also generalized the enthalpy formulation of Date [158] to the case where the material has a range of phase-change temperature. This model was validated with experimental data. From this analysis, they concluded that the solidification time is approximately $1/n$ time the no fin case, where n is the number of fins. They also pointed out that, in the central part, the flow is restricted between fins. Therefore, when the number of fins exceeds 4, half the fins can extend to only half the cylinder radius. In their subsequent work [159], they pointed out the necessity to include the effect of circumferential heat flow through the tube wall for higher values of Biot numbers in order to correctly predict the heat-transfer behavior. For lower Biot numbers, addition of fins makes the surface heat flux more uniform, whereas for higher Biot numbers the addition of fins improves the magnitude of the surface heat flux and appreciably reduces the solidification time. For a given quantity of heat to be extracted, a combination of lower Biot number and higher Stefan number is recommended for the uniform extraction of heat. The same team [160] also investigated transient behavior of a finned-tube latent heat thermal storage module with thin circumferential fins. Numerical results indicate an appreciable enhancement in the energy storage process with the addition of fins in the module.

Lamberg and Sirén [161–164] developed an analytical model for analysis of the melting and solidification in a finned PCM. The results of the derived analytical model were compared to numerical results of a two-dimensional model solved numerically by means of the effective heat capacity method and enthalpy method. The two-dimensional results were compared to simplified one-dimensional results in order to find out the accuracy of the simplified analytical model. The results of the experimental work were then compared to the numerical results calculated using the effective heat capacity method and enthalpy method, in order to find out the accuracy of different numerical methods. The results show that the analytical models give a satisfactory estimate of fin temperature and of the solid–liquid interface.

Castell et al. [165] studied both experimentally and numerically the impact of external longitudinal fin on PCM module placed in a water tank working with a solar heating system. The geometry of the PCM modules is the same used in an other experimental work done by the authors [166,167] but with added fin on the PCM module. Experimental work was carried out to determine natural convection heat-transfer coefficients for PCM modules. To compare the behavior of the system using finned PCM modules with another one without fins, two numerical codes were implemented. The results obtained from the simulation were compared with the experimental ones to validate the numerical codes. Based on those experimental results, useful Nusselt correlations in function of Rayleigh number were found to evaluate the natural convection heat-transfer coefficient for that specific geometry.

Reddy [168] modeled a PCM-water solar system consisting of a double rectangular cross section enclosure where the top enclosure is filled with paraffin wax and the bottom is filled with water. The numerical modeling has been carried out using the commercial CFD software FLUENT. The geometry modeling and mesh were generated in GAMBIT. An enthalpy porosity technique was used in FLUENT for modeling the solidification/melting process. In this technique, the mushy zone is modeled as a pseudo porous medium in which the porosity decreases from 1 to 0 as the material solidifies. Simulation results indicate that an optimal number of fins should be used to optimize the overall system performance.

Gharebaghi and Sezai [169] investigated the enhancement of energy storage rate of a thermal energy storage unit filled with a PCM by inserting a fin array. Heat is transferred to the unit through the container walls, to which fins are attached; a commercial paraffin wax is stored between the fins. A mathematical model, based on the finite-volume method for a two-dimensional domain, is developed for solving the melting problem. A fixed-grid method is used to simulate the melting of the PCM. The interface between

the solid and the melt is modeled as a porous medium. Transient simulations have been performed on non-uniform grids for different fin and PCM layer thicknesses. For horizontal and vertical arrangements of modules, it was observed that for high temperature differences, the heat-transfer rate can be increased as much as 80 times by adding a fin array. The minimum enhancement rate was 3 times, which was achieved with widely spaced fins. It was also observed that the Nusselt number is higher for vertical modules arrangement compared with that of horizontal modules for all fin spacings and temperature differences.

Ismail et al. [170] studied a thermal numerical model for the solidification of PCM around a radially finned tube with a constant wall temperature. Their model was based on a pure conduction formulation and the enthalpy method. Numerical simulations were performed to investigate the effects of the number of fins, fin thickness, fin material, aspect ratio of the tube arrangement and the tube wall temperature. The study shows that the geometrical aspects have strong influences on the time for complete solidification and on the solidification rate. Also, the tube material as well as the tube wall temperature affect the time for complete solidification. The same team [171], following the same procedure, analyzed the behavior of the solidification of a PCM around a vertical axially finned isothermal cylinder. Their numerical model was validated by experimental data. From this analysis, the authors suggested that a metallic tube fitted with four or five fins of constant thickness equal to the tube wall thickness and of radial length around twice the tube diameter should be the best compromise solution between efficiency, increase in the heat flow rate and the loss of available storage capacity.

Kayansayan and Ali Acar [172] modeled the formation of ice around a finned-tube heat exchanger. Due to the small temperature difference between the tube outside surface and the PCM (less than 5 °C), natural convection is very weak and even more hampered by the presence of vertical fins. The validity of their model was established by comparison with Lacroix [154] and an experimental setup.

The thermal control of portable electronic devices, with their intermittent operation, is well adapted to PCM utilization. However, careful optimization needs to be done to insure the adequate sizing and consistent behavior under realistic operational condition.

Akhilesh et al. [173] developed a model of a composite heat sink composed of vertical arrays of fins surrounded by phase-change material. It should be noted that heat load was coming from the top of the heat sink. This heat sink was to be used for cooling electronic package below a set point temperature. This model provides a thermal design procedure for proper sizing of the heat sink, for maximizing energy storage and for operation time. Based on a scaling analysis of the governing two-dimensional unsteady energy equations, a relation between the critical dimension for the heat sink and the amount of PCM used was developed.

Shatikian et al. [105,174,175] explored numerically the process of melting of a phase-change material (PCM) in a heat storage unit with internal fins open to air at its top. The phase-change material, paraffin wax, was stored between the fins. Transient three and two-dimensional simulations were performed using FLUENT 6.0, yielding temperature evolution in the fins and the PCM. Using a dimensional analysis to generalize their results, they have shown that within the same geometry, the Nusselt number and melt fraction depend on the product of the Fourier and Stefan numbers. For relatively wide vertical PCM layers, the Rayleigh number must also be included, to take into account the effects of convection at advanced stages of the melting process.

Běhunek and Fiala [176] also modeled a heat sink for electronic package including PCM based on the work of Nayak et al. [177]. In their configuration, the inorganic crystalline salt acting as PCM was placed in a chamber right over the chip. This chamber was put in contact with fin cooled by forced convection of air. They first created an analytical description and a solution of heat transfer, melting and freezing process in 1D and compared their solution to the numerical solution obtained, through a FEM solution in ANSYS software, of a real 3D cooler. In addition, results of 3D numerical solutions were verified experimentally.

Saha et al. [178] also made an analysis of a similar system and geometry both experimentally and numerically. Their experimental setup consisted of an electrical heater to simulate the electronic chips with the heat sink filled with eicosane above. The governing equations of their numerical model follow a single domain approach where both fluid flow and heat-transfer equations are solved simultaneously. The fin, heater, and substrate materials are assigned very high viscosity and melting points, which ensures that they remain solid. In consequence, a common set of governing conservation equations for both the solid and liquid regions can be used [177]. An optimal fin fraction of 8% was found. This was attributed to convection cells in the molten region of the PCM present at a large volume fraction of PCM but otherwise suppressed. It was also found that a large number of narrow cross section fins is preferable, since it improves the thermal contact for a same volume.

Kandasamy et al. [179] have also studied a similar heat sink experimentally and numerically. Results show that increased power inputs enhance the melting rate as well as the thermal performance of the PCM-based heat sinks until the PCM is fully melted. A three-dimensional computational fluid dynamics model was used to simulate the problem. To describe the PCM–air system with a moving internal interface but without inter-penetration of the two fluids, the volume-of-fluid model has been used successfully [180] and showed good agreement with experimental data. The same team [181] using the same approach explored the effect of orientation on performances. They concluded that orientation has a minimal effect in their configuration.

In an original approach, Wang et al. [182] created a constructal rule for the design of fins in PCM application. Constructal optimization of heat conduction with phase-change mimics the growth of plants in nature. The high conductivity material is treated as the plant root, and the PCM acts as the soil. The product of thermal conductivity and temperature gradient integration over time in the whole melting time interval of the PCM is taken as the criterion to determine the arrangement position of the high conductivity material. Its physical meaning is the quantity of total heat transported during the melting time interval. The generation rule of constructal optimization of heat conduction with phase change is to grow the high conductivity material at the position with the maximum total heat transported during the time interval. The degeneration rule is to withdraw the high conductivity material at the position with minimum total heat transported during the time interval. Comparison between constructural and man-made shapes confirm that constructal ones are superior in melting time and in the average cold release power.

Table 6 presents the synthesis for finned surfaces.

4.6. Porous and fibrous materials

Erk and Dudukovic [183] modeled and experimented with a PCM consisting of n-octadecane retained by capillary forces in a porous silica support. It optically changes from opaque to semitransparent when the wax melts, thereby allowing the melt front within the bed to be tracked. This property and the outlet temperature were compared with the model. Measured outlet temperature compares qualitatively with model predictions. The model quantitatively predicts melt front movement in the first 60%

Table 6
Models for finned surfaces.

Model	Material	Numerical formulation		Comment	Validation
Sasaguchi et al. [152,153]			3D	Performance independent of geometry only surface area	Yes
Lacroix [154]	n-Octadecane	FD	2D	An analytic 1D model is also produce	Yes
Lacroix and Benmadda [155]		FG			
Zhang and Faghri [156]		FD FG	2D	Validation of semi-analytic result of [231]	Numerical Lacroix [154] Kays and Crawford [232]
Velraj et al. [157,159,160]	Paraffin RT 60 [157] LiF–MgF_2 [160]	FD FG	2D	Phase-change material kept inside a longitudinal internally finned vertical tube	Yes [157] 159] num. [155] [160] num. [233]
Lamberg and Sirén [161–164]	Paraffin	FE	2D	Analytical model validated	Yes
Castell et al. [165,234]	Sodium acetate trihydrate with graphite	A		Horizontal and vertical fins around circular vertical cylinder	Yes
Reddy [168]	Paraffin wax	MM	2D	Double rectangular enclosure where the top enclosure is filled with paraffin wax and the bottom is filled with water	Experimental [252]
Gharebaghi and Sezai [169]	Paraffin RT27	FD FG	2D	Slabs containing paraffin and metal fins made of aluminum	Yes
Ismail et al. [170,171]	Ice [105] Paraffin [174]	FD	2D	Radially finned horizontal tube [170] Axially finned vertical tube [171]	Yes [171]
Kayansayan and Acar [172]	Ice	FD FG	2D	Radially finned horizontal tube	Numerical Lacroix [154] Zhang and Faghri [156]
Akhilesh et al. [173]	n-Eicosane	FD FG	2D	Array of vertical fins	Numerical Bejan [235]
Shatikian et al. [105,174,175]	Paraffin wax RT25		2D 3D	Array of vertical fins	Numerical [105]
Běhunek and Fiala [176,163]	$CaCl_2{\cdot}6H_2O$	1D	3D	Also analytical 1D	Yes

of the bed. Discrepancies between the model and experiments are linked to significant heat losses in the small insulated bench-scale apparatus used for the experiment.Mesalhy et al. [184,185] studied numerically and experimentally the effect of porosity and thermal properties of a porous medium filled with PCM. In their model, the governing partial differential equations describing the melting of phase-change material inside porous matrix were obtained from volume averaging of the main conservation equations of mass, momentum, and energy. Due to the huge difference in thermal properties between the phase-change material and the solid matrix, two energy equations model was adopted to solve the energy conservation laws. This model can handle local thermal non-equilibrium condition between the PCM and the solid matrix. Finite-volume technique in conjunction with numerical grid generation based on body fitted coordinate transformation has been adopted. From their model, it was found that the best technique to enhance the response of the PCM storage is to use a solid matrix with high porosity and high thermal conductivity. The same team [186] investigated the properties of graphite foams infiltrated with phase-change materials. The geometry studied was two concentric cylinders, the inner being kept at a constant temperature while the outer one is filled with foam/PCM matrix. The model has been validated by applying it on the case described by Khillarkar et al. [187] and has shown to be in good agreement. Model results indicate that estimated value of the average output power using carbon foam of porosity 97% is about five times greater than that for using pure PCMs.

Fukai et al. [188,189] modeled and experimented the use of carbon-fiber combined with n-octadecane. Carbon fibers were added to improve the thermal conductivities of phase-change materials packed around heat-transfer tubes. The transient thermal responses improved as the volume fraction of the fibers and the brush diameter increased. However, these do not further improve when the diameter of the brush is larger than the distance between the tubes due to thermal resistance near the tube walls. The discharge rate using the brushes with a volume of one percent was about 30% higher than that using no fibers. In the charge process, the brushes prevent natural convection. Still, the charge rate with the brushes is 10–20% higher than that with no fibers. A heat-transfer model describing anisotropic heat flow in the composite was numerically solved. The calculated transient temperatures agreed well with the experimental data. A simple model was also developed to predict the heat exchange rate between the composite and the heat-transfer fluid. Hamada et al. [190] compared experimentally and numerically the thermal behavior of carbon chip and carbon brush. The carbon-fiber chips are efficient for improving the heat-transfer rate in PCMs. However, the thermal resistance near the heat-transfer surface is higher than that for the carbon brushes. As a result, the overall heat-transfer rate for the fiber chips is lower than that for the carbon brushes. Consequently, the carbon brushes are superior to the fiber chips for the thermal conductivity enhancement under these experimental conditions.

Elgafy and Lafdi [191] studied experimentally and analytically the behavior of nanocomposite carbon nanofibers filled with paraffin wax. An analytical model was introduced based on a one-dimensional heat conduction approach to predict the effective thermal conductivity for the new nanocomposites. Their findings showed good agreement with the experimental data of the authors and of Lafdi and Matzek [192].

Frusteri et al. [193] studied experimentally and numerically thermal conductivity and charging–discharging kinetics of inorganic PCM44 containing carbon fibers. A numerical model, based on the enthalpy formulation and on an implicit finite-difference method, has been developed to predict the one-dimensional heat-transfer diffusion of a PCM containing carbon fibers. The results obtained by use of this model were satisfactory compared to experimental results. Authors also pointed out that the values of thermal conductivity calculated by Fukai's method are significantly different from those measured experimentally. This was probably caused by a reduction of the thermal conductivity of the composite material near the heat-transfer surface due to both the wall thermal resistance and the contact thermal resistance [190].

The synthesis for porous and fibrous materials is given in Table 7.

Table 7
Models for porous and fibrous materials.

Model	Material	Numerical formulation		Comment	Validation
Erk and Dudukovic [183]	n-Octadecane	MM	1D	Second law efficiency calculated	Yes
Mesalhy et al. [184,185]		FD FG	2D	Carbon foam impregnated with PCM	Khillarkar et al. [187]
Fukai et al. [188,189]	n-octadecane	FD FG	2D	Carbon-fiber brushes in PCM	Yes
Hamada et al. [190]	n-octadecane	FD FG	2D	Carbon-fiber chips in PCM	Yes
Elgafy and Lafdi [191]	Parafin wax	A	1D	Carbon nanofibers in paraffin wax	Lafdi and Matzek [192,191]
Frusteri et al. [193]	37:26:38 NH_4NO_3 $Mg(NO_3)_2 \cdot 6H_2O$ $MgCl_2 \cdot 6H_2O$		2D	Carbon fibers in PCM	Yes

4.7. Slurry

Like porous and fibrous material, slurries increase heat-transfer performance and capacity of fluid. This enhancement improves the overall efficiency of cooling or heating system. Reader should consult the review of Zhang et al. [194] to learn more about properties and applications of phase-change material slurries.

This research field was first explored by Charunyakor et al. [195]. They formulated a model for heat transfer of microencapsulated phase-change material slurry flow in circular ducts. Heat generation or absorption due to phase change in the particles was included in the energy equation as a source term. The enhancement of thermal conductivity due to the particle/fluid interactions was also taken into consideration. Results of this model have demonstrated that Stefan number and PCM microcapsule concentration are the most important parameters for the system performances.

Zhang and Faghri [196] studied laminar forced convection heat transfer of a microencapsulated phase-change material in a circular tube with constant heat flux. Melting in the microcapsule was solved by a temperature transforming model instead of a quasi-steady model. This model was validated with results of Charunyakorn et al. [195] and Goel et al. [197]. This analysis pointed out that the most significant reason for the large difference between Goel et al. [197] experimental results and Charunyakorn et al. [195] numerical results is that melting takes place over a range of temperatures below the melting point. It also put into evidence the importance of shell heat-transfer properties to explain this discrepancy.

Alisetti et al. [198,199] introduced an effective heat capacity model for heat transfer in PCM slurries. Their objective was to address the shortcoming of previous models using complicated source terms or special analytical techniques or variation of the specific heat of material with temperature. This new formulation was easier to implement in standard computer fluid dynamic packages.

Roy and Avanic [200] developed a turbulent heat-transfer model based on the effective specific heat capacity for PCM slurry in a circular tube with constant wall heat flux. Their model was compared with previously published numerical [237,238] and experimental data [239–241]. It demonstrated that the bulk Stefan number, the melt temperature range, and the degree of subcooling are the driving parameters of the system.

Hu and Zhang [201] presented an analysis of the forced convective heat-transfer enhancement of microencapsulated phase-change material slurries flowing through a circular tube with constant heat flux. The model used an effective specific heat capacity and was validated with the results of Goel et al. [197]. It was found that the conventional Nusselt number correlations for internal flow of single phase fluids are not suitable to accurately describe the heat-transfer enhancement with microencapsulated phase-change material suspensions, and a modification is introduced that enables evaluation for the convective heat transfer of internal flows. Results from the model show that Stephan number and volumetric concentration of microcapsules are the most important parameters governing the heat-transfer enhancement of phase-change slurries. However, initial supercooling, phase-change temperature range and microcapsule diameter also influence the degree of heat-transfer enhancement. The enhancement increases with decreasing initial supercooling and/or phase-change temperature range, and with microcapsule diameter. Therefore, the degree of enhancement in a small-diameter tube may be better than in a large pipe for a given phase-change slurry.

Hao and Tao [202] developed a model for simulation of the laminar hydrodynamic and heat-transfer characteristics of suspension flow with micro–nano-size PCM particles in a microchannel. The model solves simultaneously the two-phase equations of mass, momentum, and energy. This has allowed the investigation of heat-transfer enhancement limits, due to non-thermal equilibrium melting of PCM, existence of a particle-depleted layer, particle–wall interaction, phase-change region propagation, and local heat-transfer coefficients for both constant wall heat flux and constant wall temperature boundary conditions. The same group [203] developed a two-phase, non thermal equilibrium-based model for the numerical simulation of laminar flow and heat-transfer characteristics of PCM slurry in a microchannel. The model was validated against the experimental results of Goel et al. [197]. The results show that for a given Reynolds number, there exists an optimal heat flux under which the effectiveness is the highest.

Ho et al. [204] examined the effects of wall conduction on the heat-transfer characteristics of solid–liquid phase-change material suspension flow. A mixture continuum approach was adopted in the formulation of the energy equation, with an enthalpy model describing the phase-change process in the phase-change material particles. From numerical simulations via the finite-volume approach, it was found that the conduction heat-transfer propagating along the pipe wall resulted in significant preheating of the suspension flow in the region upstream of the heated section, where melting of the particles may occur and therefore the contribution of the latent heat transfer to convection heat dissipation over the heated section was markedly attenuated.

Inaba et al. [205] studied the fluid flow and heat-transfer characteristics for Rayleigh–Bénard natural convection of non-Newtonian phase-change material. From their model, they found that Rayleigh number, Prandtl number and aspect ratio were the most important factors for evaluating the natural convection in enclosures for most of Newtonian and non-Newtonian fluids. However, some modifications are necessary for evaluating the natural convection in a PCM slurry. In consequence, a modified

Table 8
Models for Slurries.

Model	Material	Numerical formulation		Comment	Validation
Charunyakor et al. [195]		FD	1D	Circular ducts	Ahuja [236]
Zhang and Faghri [196]		FD FG	1D	Circular tubes, constant heat flux	Experimental Goel et al. [197]
Alisetti et al. [198,199]		CFD		Effective heat capacity	
Roy and Avanic [200]	10% n-hexadecane in water	FD FG	3D	Turbulent heat transfer	Numerical Petukhov [237] Sparrow [238] Experimental Hartnett [239] Choi [240,241]
Hu et al. [201,226]		FD FG	2D	Circular tubes, constant heat flux	Experimental Goel et al. [197]
Ho et al. [204]		FD FG		Micro and nano particles	Experimental [197] Numerical [195,196]
Inaba et al. [205,206]	30:5:65 Parafin surfactant water	FD FG	2D	Natural convection, Newtonian and non-Newtonian fluids	Yes Numerical Vahl Davis and Jones [242] Ozoe and Churchill [243]
Cassidy [207]	Octacosane	FD FG	2D	Mixed convection	Yes
Royon and Guiffant [208]		FD FG	1D	Millimetric particles in oil	Numerical Bird et al. [244]
Sabbah et al. [209]		CFD	3D	3D single phase flow, FLUENT	Experimental Goel et al. [197]
Kuravi et al. [210]		FE	3D	Bulk fluid with adaptative specific heat	Experimental Goel et al. [197]
Zhang et al. [211,212]		FD FG	2D	Analogy with thermal sources	Charunyakorn et al. [195] Alisetti and Roy [199]
Sun et al. [213]	Paraffin wax		2D	Neutrally buoyant ceramics	Experimental Jones et al. [118]

Stefan number was defined to address this issue. The same team [206] produced a two-dimensional numerical simulation of natural convection in a rectangular enclosure with non-Newtonian PCM microcapsulate slurry. The formulation of the numerical model has been done using the finite-volume method. This study has demonstrated that heat-transfer coefficients of the PCM slurry with phase change are higher than those without phase change. It was found that the natural convection effect is intensified, and the heat transfer is enhanced in the case of the PCM slurry, due to the contribution of the latent heat transfer.

Cassidy [207] studied numerically and experimentally a micro PCM fluid in a circular tube with mixed convection. The PCM was octacosane encapsulated by a polyethylene shell to form a spherical particle with an average diameter of 20 μm. The micro PCM particles were suspended in a 50/50 ethylene glycol water mixture. Experimental measurements were made of the tube outer wall at the top and bottom of the copper tube. Numerically an incompressible flow model was used with an Eulerian–Eulerian method to solve the two-phase momentum and energy equations. The numerical model was validated using experimental data of single phase flow with mixed convection available in the literature and was also verified and thermal results of both single phase and two-phase flow from the experimental work of the same author.

Royon and Guiffant [208] constructed a model describing the thermal behavior of slurry of phase-change material flow with millimetric particles dispersed in oil in a circular duct. They formulated a phenomenological equation which takes into account the heat generation due to phase change in the particles. A plateau of the temperature appeared in all of the simulations where the PCM particles were considered. The length of this plateau is strongly dependent on both the weight fraction of the particles and the duct wall temperature.

Sabbah et al. [209] has investigated the influence of micro-encapsulated phase-change material on the thermal and hydraulic performance of micro-channel heat sinks. They developed a three-dimensional, one-phase, laminar flow model of a rectangular channel using water slurry of MEPCM with temperature dependent physical properties. The conservation equation was solved using FLUENT 6.2. The numerical results have been compared to experimental data of Goel et al. [197] once adapted for the circular geometry of this experiment. The model results showed a significant increase in the heat-transfer coefficient that is mainly dependant on the channel inlet and outlet temperatures and the selected PCM melting temperature. The enhancement is higher for low concentration of PCM in slurry due to the increase of slurry viscosity with its concentration.

Kuravi et al. [210] produced a numerical investigation of the performance of a nano-encapsulated phase-change material slurry in a manifold micro-channel heat sink. The slurry was modeled as a bulk fluid with varying specific heat. The temperature field inside the channel wall is solved three dimensionally and is coupled with the three-dimensional velocity and temperature fields of the fluid.

Zhang et al. [211] analyzed the convective heat-transfer enhancement mechanism of microencapsulated PCM slurries based on the analogy between convective heat transfer and thermal conduction with thermal sources. The heat-transfer enhancement for laminar flow in a circular tube with constant wall temperature is analyzed using an effective specific heat capacity model. This model was validated by comparison with the result of Charunyakorn et al. [195] and Alisetti and Roy [199]. The numerical simulation results have pointed out the Stephan number and the phase-change temperature range as the most important parameters influencing the Nusselt number fluctuation profile of phase-change slurry. The fluctuation amplitude increases with decreasing phase-change temperature range. The fluctuation amplitude and range increase with decreasing Stephan number when phase-change happens. Later, members of the same team [212] studied experimentally and numerically characteristics of microencapsulated PCM flowing in a circular tube. The enhanced convective heat-transfer mechanism was analyzed by using the

enthalpy model. Three kinds of fluid–pure water, micro-particle slurry and MPCMs were numerically investigated. They had essentially reached the same conclusions.

Using the same setup as Jones et al. [119], Sun et al. [213] studied the behavior of slurry composed of neutrally buoyant ceramic hollow spheres suspended in a paraffin wax. The numerical analysis employed a particle-diffusive model and the enthalpy method. Reasonable agreement was obtained between the experiments and numerical predictions. Nevertheless, flow and heat-transfer characteristics were greatly altered due to the presence of the solid particles and that the particle-diffusive model was insufficient to describe the particle migration during melting.

A synthesis of the numerical study of slurries is provided in Table 8.

5. Conclusion

5.1. Content

This paper presented an exhaustive review of numerical methods applied to the solutions of heat-transfer problems involving phase-change materials for thermal energy storage. The review is a model collection of fundamental and most recent works published on the subject. This survey is organized according to the problem geometry (Cartesian, spherical, and cylindrical) and specific configurations or applications (packed beds, finned surfaces, porous and fibrous materials, slurries). The authors do not claim anything about the completeness of the review as some papers may have been unfortunately neglected. The authors apology for any crucial omission and welcome all authors to contact them to complete the review.

5.2. Analysis: numerical issues and validation

As a general conclusion, one can readily observe that the older studies all had experimental counterparts to validate the modeling of the problem with an appropriate set of equations and the subsequent formulation of a numerical method to solve the relevant sets of discretized equations. Many of these early studies also involved analytical solutions used to validate the model for selected problems that admit closed-form solutions.

As time passes, the authors rely more and more on other studies, mostly other numerical studies, to validate their own numerical results. And it is somewhat interesting to mention that among the 250+ references cited here, in only one the authors stated that the results were not "in good agreement with those found in the references". Many of the recent studies discuss their results qualitatively only as the comparison with a graph taken from a publication may be somehow hazardous.

In recent studies, the proportion of analyses which rely on commercial codes increases and the discussions that pertain to stability, convergence, grid independence and other related numerical issues diminishes.

On the other hand, we found that some laboratories are involved in LHTES for decades and in these labs there is a mature culture of experimental, analytical, and numerical methods for the analysis.

5.3. Analysis: type of materials and configurations

We would like to warn readers about the risk involved when extrapolating from numerical and experimental studies and making general conclusion from them. For example, convection is strongly sensitive to the geometry and the size of the enclosure as to the viscosity and thermal conductivity of PCM. Thermal conductivity of the enclosure and the PCM solid–liquid density and conductivity contrasts also influence the thermal behavior in important and counter-intuitive ways.

There is an incentive to mix several materials with different phase-change temperature to allow for more heat recovery. Packed beds, finned geometries, porous and fibrous material-based applications, and slurries are the particular configurations for most studies that pertain to systems involving PCMs. The latter receives more attention these days as a result of the incentive to study nano-heat transfer in OECD countries.

However, it would have been interesting in these studies to discuss the issue of pumping power or the effect of the micro- or nano-capsules of PCMs on the apparent or effective viscosity of the fluids. None of the authors mention this critical issue when it comes to establish the net energy balance of operation.

Moreover, in several studies, carbon fibers are used to enhance conduction in PCMs (it is a well known fact that their average conductivity is poor) but these studies are silent about the energy cost of production of those fibers.

Another important aspect often neglected when modeling LHTES is the impact of thermal dilatation of PCM, which must be taken into account into the conception of experimental and operational systems. In both case, geometry differs from the idealized version used in most models, with poorly documented impact on performances.

5.4. Analysis: economic impact

This issue is not treated at all in any of the paper. The use of a PCM-based system compared to a standard sensible heat system is not discussed. The whole issue of storage in a technico-economical context is not found in the reviewed papers.

5.5. Concluding remarks

Models are now established for most applications of PCM materials. In many cases, simplified models or analytic expressions or correlation functions have been developed for practical guidance in optimizing design of systems using PCMs. They should be used as guidelines when adjusting the implementation of a numerical method to be used in the design of systems.

The validation of numerical predictions should always be performed by means of appropriate experimental data. The experimental data should in turn be accompanied by a suitable uncertainty analysis while the predictions should first address the issues of stability, convergence, etc. One should also keep in mind that the so-called "governing" equations do not govern but describe the physics of the problem. This semantic distinction should avoid comments found in a paper into which the authors indicate that experiments are not in agreement with the predictions instead of the opposite.

Life cycle analysis, both economical and energetic, should be performed on systems to determine into which conditions energy storage systems involving PCMs should be used.

Despite these criticisms, the actual situation which finds climate changes, security of the supplies, and fossil fuels depletion at the heart of the economic discussions will ensure a place for PCMs in the global energy efficiency policies of the world to come.

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